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EXECUTIVE SUMMARY

SOLIDIFICATION OF LIQUID WASTE FROM THE FREON BASED DRY CLEANING PROCESS

J.P. Krasznai
Chemist
Chemical Research Department

The BNPD Services Department Freon based dry cleaning facility produces a liquid waste product which is slightly radioactive. The activity is primarily due to Cs-137 and Co-60 with a small contribution from Zr-95. The operating license of the waste management facility excludes the storage of radioactive liquids and Chemical Research were requested to recommend an acceptable disposal or storage method for the waste.

Incineration of the waste at the BNPD incinerator or cement solidification were the two options considered. Analysis of the waste showed that it contained in excess of 20% Freon-113. Incineration of this waste would result in the production of significant quantities of hydrogen fluoride and hydrogen chloride from the thermal decomposition of Freon. These gases are highly corrosive. In view of this, incineration was not considered to be a practical option. Consequently the focus in this report was directed toward solidification techniques.

The technique of emulsifying the waste liquid with water and then mixing with cement powder which has been successfully used for solidifying some types of lubricating oils did not work with the typical waste from the Freon dry cleaning operation. In an attempt to keep the organic material away from the cement particles long enough to enable hydration and therefore setting of the cement the waste liquid was first absorbed into a sorbent material. Subsequently a thin cement paste was added to this dry mixture and allowed to set. This technique produced a hard solid. The waste loading however was only 8-10% of the total weight of the solidified product. Since the activity levels in the waste are quite low a more efficient immobilization scheme is recommended to BNPD Services Department. The first step

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involves absorption of the waste liquid into an absorbent material. The resulting dry mixture in a suitable container should satisfy the requirements of the waste storage facility. When a permanent waste disposal site becomes available and if the activity levels in the waste are still detectable, the dry mixture together with its container can then be encapsulated in cement.

Although, the focus of the work presented in this report is on the solidification option, incineration of the waste may be possible if the Freon content is reduced to levels at which corrosion is no longer a concern. Some additional research is suggested to determine the extent to which Freon levels can be reduced and the nature of the resulting by-product.

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To: Mr. G.H. Williams
Manager
BNPD - Services Department

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J.P. Krasznai

The operating license of the BNPD-S radioactive waste management facility does not permit the storage of radioactive liquids. Samples of Freon based waste have been analyzed and two solidification methods for these samples were investigated in this work. Waste from the commissioning of the dry cleaning facility contains in excess of 96% Freon 113 and it is recommended that this waste be redistilled to recover the Freon. The preferred immobilization technique involves absorption of the waste into a porous medium. This should be adequate for storage purposes. When disposal facilities are available and if the activity of the waste is measurable then the mixture together with its container can be encapsulated in cement. Incineration of the waste is expected to produce corrosive gases as a result of the thermal decomposition of Freon 113 and is not recommended unless the Freon content can be substantially reduced.

INTRODUCTION

The Bruce Nuclear Power Development (BNPD) Services Department uses Freon 113 based dry cleaning facilities in its laundries. Freon 113 is 1,1,2-trichloro, 1,2,2-trifluoro ethane a low boiling (48°C) nonflammable liquid. In the dry cleaning process the Freon is mixed with detergent (1% HMC) and water (1%) /1/. The by-product of the dry cleaning operation is a viscous heterogeneous liquid composed of particulate and two immiscible liquids. Periodically this waste liquid which is contaminated with small quantities of Cs-137, Co-60 and Zr-95, must be drained from the

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dry cleaning machine and is presently stored at BNPD-S. However the operating license for the BNPD-S waste management site excludes the storage of radioactive liquids. Consequently a more suitable method of long term storage is required/2/.

Two options were considered for the treatment of the waste sludge:

(a) incineration of the sludge at the BNPD-S incinerator,
(b) solidification of the sludge using cement.

DISCUSSION

Five samples of Freon waste received from BNPD-S were analyzed by Analytical Services for Freon content, water content dissolved and suspended solids. The results (Table 1) showed that all of the samples contained in excess of 20% Freon 113 and two of the samples contained 96% and 98% Freon 113, respectively. These high Freon content samples (>95%) were from waste generated during the commissioning runs of the dry cleaning machines. In view of the significant quantities of Freon 113 in the waste, the incineration option was dropped because it is likely that at the operating temperature of the BNPD waste incinerator the acid gases HF and HCl, from the breakdown of Freon 113, would give rise to unacceptable corrosion problems. Furthermore, since the waste volume production rate is only 10 drums per year these corrosion concerns outweigh the need to volume reduce the waste. The focus of this work was consequently directed towards solidification methods.

Solidification of organic liquids has been the subject of investigation in this laboratory/3/ and some of the techniques were applied to Freon waste. The formulations and observations are summarized in Table 2. A technique used successfully/4/ in the US for the solidification of waste organics was tried on the Freon sludge. It involves forming an emulsion using an equal quantity of waste and water and the addition of an emulsifying agent which prevents the emulsion from coalescing. To this emulsion the filler material, gypsum or Portland Cement is added. This technique worked very well on samples A1 and D1 which were high in Freon content, but the products from samples B, C and E did not cure at all. In view of the fact that detergents are added to the Freon as part of the dry cleaning process it was thought that an emulsifying agent which is similar in action to a detergent would not be required. However products formed without the addition of emulsifying agent also did not form an acceptable product. A possible explanation for the poor product quality from samples B1, C1 and E1 may be that the cement particles become coated with organic material and consequently the hydration reaction between the cement particles and water is inhibited. This inhibition process is not significant

for samples with high Freon contents (A1 and D1) and in fact the Freon is so loosely bound in the cement matrix that on standing the solid loses all the contained Freon by evaporation over a period of five days as measured by weight loss. In an attempt at minimizing the effect of organics on the curing of cement, high alumina cement and Plaster of Paris were used as fillers because these materials tend to hydrate much faster than Portland Cement. Only the Plaster of Paris product, B5, solidified but there was some free liquid on top of the solid after curing. In summary this approach for Freon sludge solidification resulted in an acceptable product for only two of the samples tested.

The second approach was a two-step method utilizing physical absorption of the waste onto an absorbent material followed by mixing with a thin cement paste. The basic idea is to ensure that the organic material is kept away from the cement particles so that hydration and therefore setting of the cement can proceed normally. The three absorbents tested were those which were available in the laboratory and are not necessarily the best. Florco absorbent is used generally for cleaning up oil spills but has the disadvantage that it has a high affinity for water and competes for it with cement. Consequently larger quantities of water are required to satisfy the needs of both components when using Florco as the absorbing material. Sand has a relatively small capacity for the Freon sludge. Sorbent 'C' is superior to both Florco and sand because it has a higher capacity for oil (2.5 L/kg) and it does not absorb water to a large degree. It is essential however that the absorbing material be added in sufficient quantity to give a dry mix, otherwise cement setting will be inhibited. The waste loading (ratio of the weight of liquid waste to the weight of the solidified waste) is only 8-10% with this technique which is a factor of three lower than the emulsification technique applied to lubricating oils/3/.

The foregoing has shown that the waste generated by the Freon dry-cleaning facilities can be solidified in cement albeit to a low degree of waste loading. However cement solidification of this low level waste may be going further than required by the operating license. It may be sufficient to absorb the waste liquid onto an absorbent medium like Sorbent 'C' in a suitable container (steel or polyethylene drum) and storing it as a dry mixture. This will minimize the extent of dispersion of the contents should the container be damaged during storage. When a permanent disposal facility becomes available the waste can then be checked for activity level and if required, the waste and its container can be encapsulated in cement prior to disposal as radioactive waste. A formulation and a suggested procedure for the direct solidification of the waste in cement is provided in Appendix I.

CONCLUSIONS

1. At the present time, incineration of Freon based dry cleaning wastes is not recommended due to the likelihood of producing corrosive gases as a result of thermal decomposition of Freon 113, unless the Freon content is substantially reduced. It may be appropriate to operate the dry cleaning machines in a way that reduces the Freon content of the waste.

2. Some research effort should be spent in developing methods to reduce the Freon content of the waste (vacuum distillation or evaporation) and determining the nature of the final waste product with respect to ease of handling and incineration.

3. Emulsification of the waste liquid with water and the surfactant Triton X114 followed by the addition of cement, works only with the very high Freon content samples A and D. Rather than solidify this particular waste it is recommended that it be redistilled to recover the Freon.

4. Absorption of the waste into an oil absorbing material such as sorbent 'C' is the preferred method of treatment of Freon waste for storage. For final disposal, cement solidification may be required depending on the activity level.

5. If cement solidification is required, direct mixing of the waste/absorbent mixture with cement paste gives a solid product but with a low waste loading efficiency. It is preferable therefore, that the waste/absorbent mixture together with its container be encapsulated using cement in a larger diameter container.

6. At the present time, the solidification process for radioactive waste organic liquids has to be tailored to the specific waste liquid to be solidified. It is recommended that research be carried out to determine the factors affecting the solidification of organics in cement and then formulate a single process that can be applied to solidify all of Ontario Hydro's waste organic liquids.

ACKNOWLEDGEMENT

The assistance of W. McPherson in preparing the specimens is gratefully acknowledged.

Approved by:

S.H. Hawthorne

O.A. Kupcis
Manager
Chemical Research Dept

Prepared by:

John Krasznai

J.P. Krasznai
Chemist
Organic Research Section

Reviewed by:

R.W. Glass

R.W. Glass
Supervising Chemist
Organic Research Section

JPK:lg/djb

TABLE 1

	Name	Analyte 1	Analyte 2	Analyte 3	Analyte 4	Analyte 5
Name		Freon g/kg	Water Content g/kg	Susp Solids g/L	Filt Residue g/L	Sample Type
S1	Drum #154 (E)	270	80	Unfilterable	Unfilterable	63% liquid, 38% sludge
S2	Drum #16 (A)	980	4.8	0.50	4.6	Freon/Water
S3	Drum #67 (B)	430	15.9	6.7	420	Freon/Sludge/Water
S4	Drum #24 (D)	960	1.4	0.21, 0.23	4.7	Freon
S5	Composite (C)	210	231	Unfilterable	Unfilterable	Sludge

TABLE 2

FORMULATIONS FOR FREON WASTE SOLIDIFICATION

Sample	A	B									C			D	E	
Sample No.	1	1	2	3	4	5	6	7	8	9	1	2	3	1	1	2
Freon Content (g/L)	980	430	430	430	430	430	430	430	430	430	210	210	210	960	270	270
Sample Wt (g)	78	60	60	60	60	25	60	90	120	240	60	60	12	78	60	60
Water (g)	50	50	50	50	100	100	175	175	175	175	50	50	50	50	50	50
Portland Cement (g)	150	150	150	–	–	–	525	525	525	525	150	150	–	150	150	150
High Alumina Cement (g)	–	–	–	150	150	–	–	–	–	–	–	–	150	–	–	–
Plaster of Paris (g)	–	–	–	–	–	150	–	–	–	–	–	–	–	–	–	–
Emulsifier (g)	5	5	–	5	–	3	–	–	–	–	5	–	–	5	5	–
Absorbent (Type)	–	–	–	–	Florco	–	Sorbent 'C'				–	–	Sand	–	–	–
Absorbent (Wt)	–	–	–	–	–	–	15	15	15	15	–	–	–	–	–	–
Product Quality	Hard Solid	No Cure	No Cure	No Cure	Hard Solid	Hard Solid Free Liquid	Hard Solid	Soft Solid	No Cure	No Cure	No Cure	No Cure	Hard Solid Free Liquid	Hard Solid	No Cure	No Cure

NOTES: (1) Sample A from Drum #16
(2) Sample B from Drum #67
(3) Sample C from Drum #CX 84-1269
(4) Sample D from Drum #24
(5) Sample E from Drum #154
(6) Superplasticizer added to cement to assist pourability
(7) Triton X114 used as emulsifier

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APPENDIX I

PROCEDURE FOR THE SOLIDIFICATION OF WASTE DRY CLEANING SOLVENT (4.5 L SCALE)

1. Mix 0.5 L (~0.6 kg) of waste liquid with 200 g of Sorbent 'C' (Stock Code No: 929-10762) to give a dry mixture. If the mixture agglomerates into pellets it is not dry enough and more absorbing compound must be added.

2. In a separate container mix 4.5 kg Portland Cement (PC30) with 1.5 kg water. 80 mL of superplasticizer Mighty 150 (sulphonated napthalene formaldehyde) is added during mixing to keep the cement paste very fluid. A thin cement mix is required to penetrate the porous waste/absorbent mixture.

3. Pour the cement paste on top of the dry waste/absorbent mixture and mix the contents just sufficiently to ensure that all the waste is folded into the cement matrix. A minute or two on a drum roller is adequate. If superplasticizer is used, the resulting cement paste should be poured within 30 minutes otherwise the mixture will be difficult to pour and mix.

4. The heat of hydration during the curing period (~24 h) is significant and the temperature in the cement mass will be in excess of the boiling point of Freon 113. Therefore during curing the container should be periodically vented to minimize pressure buildup inside the container.